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Polyheterocycle Langmuir-Blodgett Films

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X.Q. Yang, J. Chen, P.D. Hale, T. Inagaki, T.A. Skotheim, D.A. Fischer, Y. Okamoto,
L. Samuelson, S. Tripathy, K. Hong, I. Watanabe, M.F. Rubner, M.L. denBoer

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Polyheterocycle Langmuir-Blodgett Films

X.Q. Yang, J. Chen, P. D. Hale, T. Inagaki, and T.A. Skotheim

Division of Materials Science, Brookhaven National Laboratory, Upton, NY 11973

D. A. Fischer

Exxon Research and Engineering

Y. Okamoto

Department of Chemistry, Polytechnic University, Brooklyn, NY 11201

L. Samuelsen and S. Tripathy

Department of Chemistry, Lowell University, Lowell, MA 01854

K. Hong, I. Watanabe, and M.F. Rubner

Department of Materials Science and Engineering

Massachusetts Institute of Technology, Cambridge, MA 02139

M. L. denBoer

Department of Physics, Hunter College of CUNY, New York, NY 10021

Abstract

Two types of polyheterocycle Langmuir-Blodgett films have been fabricated: (1) copolymers of pyrrole and 3-alkyl pyrrole (3-hexadecylpyrrole and octadecylpyrrole) LB films; (2) mixtures of poly(3-alkyl thiophene) and stearic acid LB films. The orientation of single- and multi-layer films on platinum substrates have been studied by Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy which also provides information about interaction between the aromatic groups and the metallic substrate. The alkylsubstituted pyrrole monomers form highly ordered multi-layer LB films with the hydrocarbon chains perpendicular to the substrate, while the LB films of copolymers of pyrrole and alkylsubstituted pyrrole are more disordered. In the case of mixtures of poly(3-alkyl thiophene) and stearic acid LB films, the hydrocarbon chains of the stearic acid molecules are highly ordered. The poly(3-alkyl thiophene) components, on the other hand, exhibit random orientation of the thiophene moieties. The orientation of the hydrocarbon chain of the poly(3-alkyl thiophene) varies with the chain length, from random to highly ordered along the surface normal of the substrate, as the chain length changes from 4 carbon units to 18 carbon units.

Introduction

The increasing interest in organic and polymeric electroactive materials arises from their potential applications in synthetic membranes, nonlinear optical elements, sensors, and microelectronic devices. However, in contrast to inorganic materials for which sophisticated processing and characterization technologies have been established, the processing and characterization of electroactive polymeric materials are still the major stumbling blocks to their successful utilization. The Langmuir-Blodgett technique provides a rational approach for fabricating films with well defined composition, structure and thickness. Applying this technique to the



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electroactive polymers opens new approaches to the design and processing of this promising class of novel materials. Fabrication and characterization of mono- and multi- layer LB films of electrically conductive polymers is the main goal of our research.

In this paper we report on two approaches which have been recently disclosed as a means to prepare electroactive polyheterocycle LB films. They include: (1) spreading a mixture of pyrrole monomer and a surface active pyrrole derivative (3-octadecyl pyrrole or 3-hexadecyl pyrrole) onto a subphase containing an oxidizing aqueous solution of FeCl_3 to copolymerize the pyrrole and surface active pyrrole derivatives.¹ (2) spreading a mixture of a poly(3-alkyl thiophene) and surface active materials such as stearic acid ($\text{C}_{17}\text{H}_{35}\text{-COOH}$) on the purified water subphase to form an LB film of the mixture.² Detailed characterization of the molecular structure of the LB films is essential for developing techniques for system design. Several techniques have been used to study the orientational behavior of LB films, including infrared,^{3,4} Raman,⁵ and x-ray diffraction.⁶ Recently, Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy has been applied to study the monolayer LB films of arachidic acid and cadmium arachidate.⁷ In the NEXAFS technique, core level electrons are excited by the incident photons to unoccupied orbitals near the ionization threshold. The core levels of excitations discussed in this paper are those from the carbon $1s$ and sulfur $2p_{3/2}$ and $2p_{1/2}$ levels to the unoccupied σ^* and π^* orbitals. By scanning the incident photon energy and monitoring the Auger electrons resulting from the relaxation process of excitation, the empty states such as $\text{C-C } \sigma^*$, $\text{C=C } \sigma^*$, $\text{C=C } \pi^*$ and C-H^* can be identified. The resonance peaks corresponding to transitions to empty σ^* and π^* orbitals will have a maximum intensity when the electric field vector of the incident photon beam is parallel to the σ orbitals (parallel to the bond axis) and π orbitals (perpendicular to the bond axis), respectively. Using the highly polarized x-ray beam of the synchrotron radiation, the orientation of certain bonds such as C=C and C-H relative to the substrate can be determined by comparing the NEXAFS spectra collected with different angles between the E vector and the substrate.

Experimental

Pyrrole-alkyl pyrrole Copolymers

The surface active 3-alkyl pyrroles used in this study are hexadecylpyrrole (HDP) and octadecylpyrrole (ODP). The detailed procedure of the synthesis was described in earlier publications.^{1,8} The LB films were prepared on a modified Lauda film balance. For the HDP monomer films, the monolayers were spread from chloroform solutions with 0.57mg/ml HDP concentration onto a purified water subphase. The surface pressure-area isotherm is shown in figure 1. In order to make an insoluble conducting polymeric LB film, a mole ratio in excess of 300 to 1 of unsubstituted pyrrole to ODP is needed. A chloroform solution of this mixture was spread onto

a subphase containing ferric chloride. An idealized schematic of the copolymerization of 3-alkyl pyrrole and pyrrole on the LB trough is displayed in figure 2. The 3-alkyl pyrrole and pyrrole are shown to form an alternating copolymer on the air-water interface which may not always be the case. The FeCl_3 acts as both a polymerizing agent and a dopant. The structure of polypyrrole is believed to consist of a linear planar chain with pyrrole rings alternating in opposite directions along the chain.⁸ If this is indeed the preferred structure, then polymerization of an alkyl substituted pyrrole in a monolayer form would be hindered by such an arrangement as it would require that the alkyl chains pendent to the resultant polymer backbone point in opposite directions. This suggested that the addition of a bridging molecule such as an unsubstituted pyrrole might assist in the polymerization of this system.^{1,2} Detailed studies¹ showed that neither pure ODP nor unsubstituted pyrrole alone will form the electrically conductive polymer phase when dispersed from chloroform solutions onto a subphase containing FeCl_3 . An excess of unsubstituted pyrrole is needed to account for the solubility of pyrrole in water. The conditions necessary to produce electrically conductive films are obtained when the amount of pyrrole relative to ODP is very high. The highest conductivities are reached when the mole ratio of pyrrole to ODP is approximately 5000 to 1.

Poly(3-alkyl thiophene)/stearic acid Mixture Layers

Three types of poly(3-alkyl thiophenes) have been synthesized²: Poly(3-butyl thiophene) (poly-3-BT); Poly(3-octyl thiophene) (poly-3-OT) and Poly(3-octadecyl thiophene) (poly-3-ODT). They can be chemically or electrochemically polymerized. They are soluble in organic solvents but are not surface active. The LB films were obtained by spreading a mixture of the poly(3-alkyl thiophenes) and stearic acid ($\text{C}_{17}\text{H}_{35}\text{COOH}$) onto the water subphase. Figure 3 shows the components used to form a stable monolayer. The pressure-area isotherms of various poly(3-alkyl thiophenes)/ stearic acid mixtures are presented in figure 4. The mixtures form very stable monolayers on the water surface, independent of the different methods of preparing the poly(3-alkyl thiophenes). Multi-layer LB films of these systems have been prepared on Pt-coated glass slides for structure determination.

NEXAFS Studies

The NEXAFS studies were carried out on beam lines U-3 and U-14 at the National Synchrotron Light Source. The NEXAFS spectra were obtained by total electron yield detection, measuring the sample current and normalized by the current from a gold grid placed in the incident beam. The carbon *k*-edge NEXAFS spectra of hydrocarbon chains have been well studied.^{7,9} The resonance peak corresponding to the $(\text{C-H})^*$ and $\text{C-C } \sigma^*$ transition have opposite polarization

dependence. The C-H* peak will be most pronounced when the E vector of the incident beam is perpendicular to the hydrocarbon chains and the C-C σ^* peak will be most pronounced when the E vector is parallel to the hydrocarbon chains. Comparing the spectra taken at normal incidence (E parallel to the substrate) and at grazing incidence (E perpendicular to the substrate), the orientation of the hydrocarbon chains with respect to the substrate can be derived if they are highly ordered. The energies and proposed assignments of features of the alkylsubstituted pyrrole monomer and copolymer LB films are listed in table 1.

Figure 5 shows the NEXAFS spectra for the carbon *k*-edge of monolayer(A) and multi-layer(B) hexadecylpyrrole LB films. In both spectra, the (C-H)* peak has the largest intensity at normal incidence where the E vector is parallel to the substrate, so the hydrocarbon chains must be oriented close to perpendicular to the substrate. However, the monolayer spectra in (A) show a reduced polarization dependence. This could be attributed to either a disordering or tilting effect of the hydrocarbon chains. It is more likely due to the tilting effect caused by the interaction between the pyrrole head group and the Pt substrate which would make the pyrrole ring orient close to parallel to the substrate. From the second layer up, the chains orient normal to the substrate, since the pyrrole ring is no longer in contact with the substrate.

It also should be noted that the C=C π^* resonance peak (feature 1 in figure 5 (B)) is not present in Fig. 5 (A) for the monolayer film. Since there is no C=C bond in the alkyl chain, this feature is related solely to the pyrrole head group. When heterocycles are in intimate contact with a metal surface, charge transfer to the metal occurs, resulting in strong bonding or decomposition.^{10,11} This charge transfer interaction with the metal substrate results in an energy upshift of the C=C π^* feature (labelled 1' in Fig.5 (A)) which is unresolvable from the strong peak of (C-H)*, and makes the center of the combined C=C π^* and (C-H)* peak shift down.

Figure 6 shows the carbon *k*-edge NEXAFS spectra of octadecylpyrrole monomer (A) and a copolymer of pyrrole and ODP (B) monolayer LB films on Pt. The similarity of figure 6(A) and figure 5(A) indicates that the ODP monomer monolayer LB film is ordered but tilted from the surface normal similar to the HDP monomer single layer LB film. However, the polarization dependence of the spectra for the copolymer LB films has been severely reduced. This suggests that disorder has been introduced during the polymerization process. The oxidized film contains anions, which are derived from the FeCl₃ in solution. Since the anions are water soluble, their most likely position would be underneath the compact alkylpyrrole film at the air-water interface. Subsequent to transfer, their most likely position would be between the pyrrole head groups and the metal substrate. This could lead to a separation of the pyrrole moieties from the metal substrate and prevent the charge transfer interaction which occurs with intimate contact. The transition to the unaltered C=C π^* orbital (feature 1 in fig.6 (B)) is consequently observed.

Figure 7 shows the carbon *k*-edge NEXAFS spectra of LB films of poly(3-ODT)/stearic acid

(A) and poly(3-BT)/stearic acid (B) mixtures. The polythiophene is undoped. The energies and proposed assignments of the features are given in table II. The spectra for poly(3-ODT) /stearic acid in (A) show very strong polarization dependence with the highest intensity of (C-H)* peak at normal incidence. This indicates that the hydrocarbon chains of the stearic acid are highly ordered and oriented along the surface normal, as in the HDP and ODP monomer LB films. In Fig. 7 (B), the polarization dependence is still clear but somewhat reduced which can be seen by the increased intensity of (C-H)* peak at grazing incident. This indicates some kind of disordering effect. It could be due to the random orientation of the shorter alkyl chains (4 carbon units compared to 18 carbon units in Fig. 7(A)) in the 3-butylthiophene. For the longer alkyl chain compounds, such as octadecylthiophene, the alkyl chains might be oriented along the same direction (normal to the substrate surface) as the hydrocarbon chains of the stearic acid, resulting in spectra exhibiting a higher degree of ordering. Results available to date indicate that the poly(3-alkyl thiophenes) are randomly distributed within layers of highly ordered stearic acid molecules. A periodicity of 50 Å for the bilayer spacing is maintained throughout the LB films as determined by x-ray diffraction.⁷ A proposed model on the microstructure of this mixed system is illustrated in figure 8.

Conclusion

Two types of polyheterocycle Langmuir-Blodgett films have been fabricated. The pyrrole/octadecylpyrrole copolymers exhibit disordering compared with the highly ordered alkyl substituted pyrrole monomer LB films. In the monomer films, the hydrocarbon chains are highly ordered and oriented along the surface normal for multi-layer films. A strong interaction between the pyrrole head groups and the Pt substrate was observed in the single layer monomer LB films. The poly(3-alkyl thiophene)/ stearic acid LB films show a high degree of ordering with the hydrocarbon chains of the stearic acid oriented along the surface normal. The hydrocarbon chains of poly(3-ODT) are also oriented along the surface normal in contrast with the random orientation of the shorter chains of the poly(3-BT).

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TABLE I
Energies and proposed assignment of features
in the C 1s spectrum of Hexadecylpyrrole (HDP) LB films

HDP monolayer				HDP multi-layer			Assignment (final orbital)	
#	E (eV)	Intensity 90° 20°		E (eV)	Intensity 90° 20°		Ring	Hydrocarbon chain
1				285.5	sh	sh	π^* 3b ₁ (C=C)	
1'	287.5*						π^* 3b ₁ (C=C)	
2	288.5	s	m	288.5	s	m	[π^* 2a ₂ (C=C)]	π^* (CH ₂)
3	294	s	s	294	m	s	σ^* (C-C)	σ^* (C-C)
4	298.5	w	w	298.5	w	w	σ^* (C-C)	σ^* (C-C)
5	303	wm	m	303	wm	m	σ^* (C=C)	

s strong; m medium; wm weak medium; w weak; sh shoulder

* energy upshifted from 285.5 eV due to charge transfer interaction.

TABLE II

Energies and proposed assignment of features in the
C 1s spectrum of Polythiophene/Stearic Acid LB film

Assignment (final orbital)					
#	E (eV)	Intensity 90° 20°		Ring	Hydrocarbon chain
1	285.5	sh	sh	π^* 3b ₁ (C=C)	
2	288.5	s	m	[π^* 2a ₂ (C=C)]	π^* (CH ₂)
3	294	s	s	σ^* (C-C)	σ^* (C-C)
4	298.5	w	w	σ^* (C-C)	σ^* (C-C)
5	303	w	w	σ^* (C=C)	

s strong; m medium; wm weak medium; w weak; sh shoulder

* energy upshifted from 285.5 eV due to charge transfer interaction.

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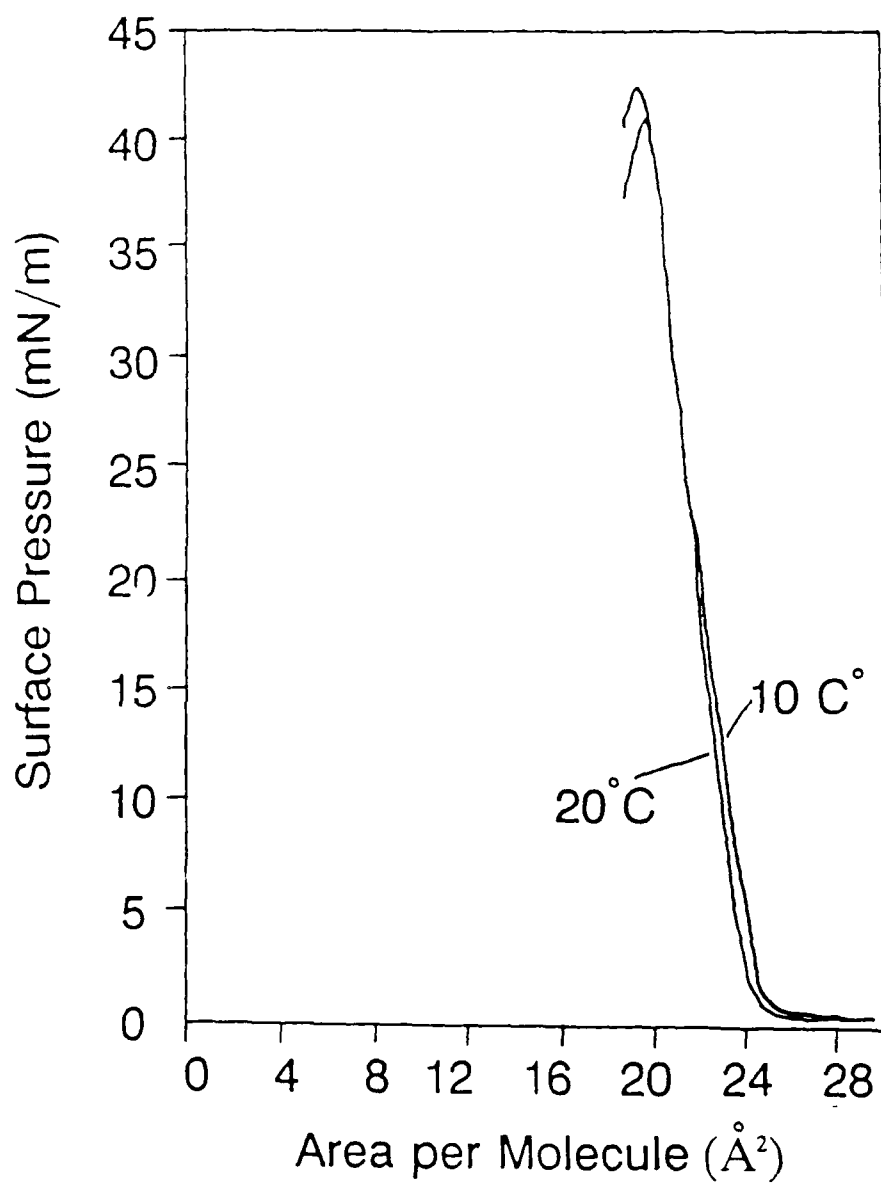
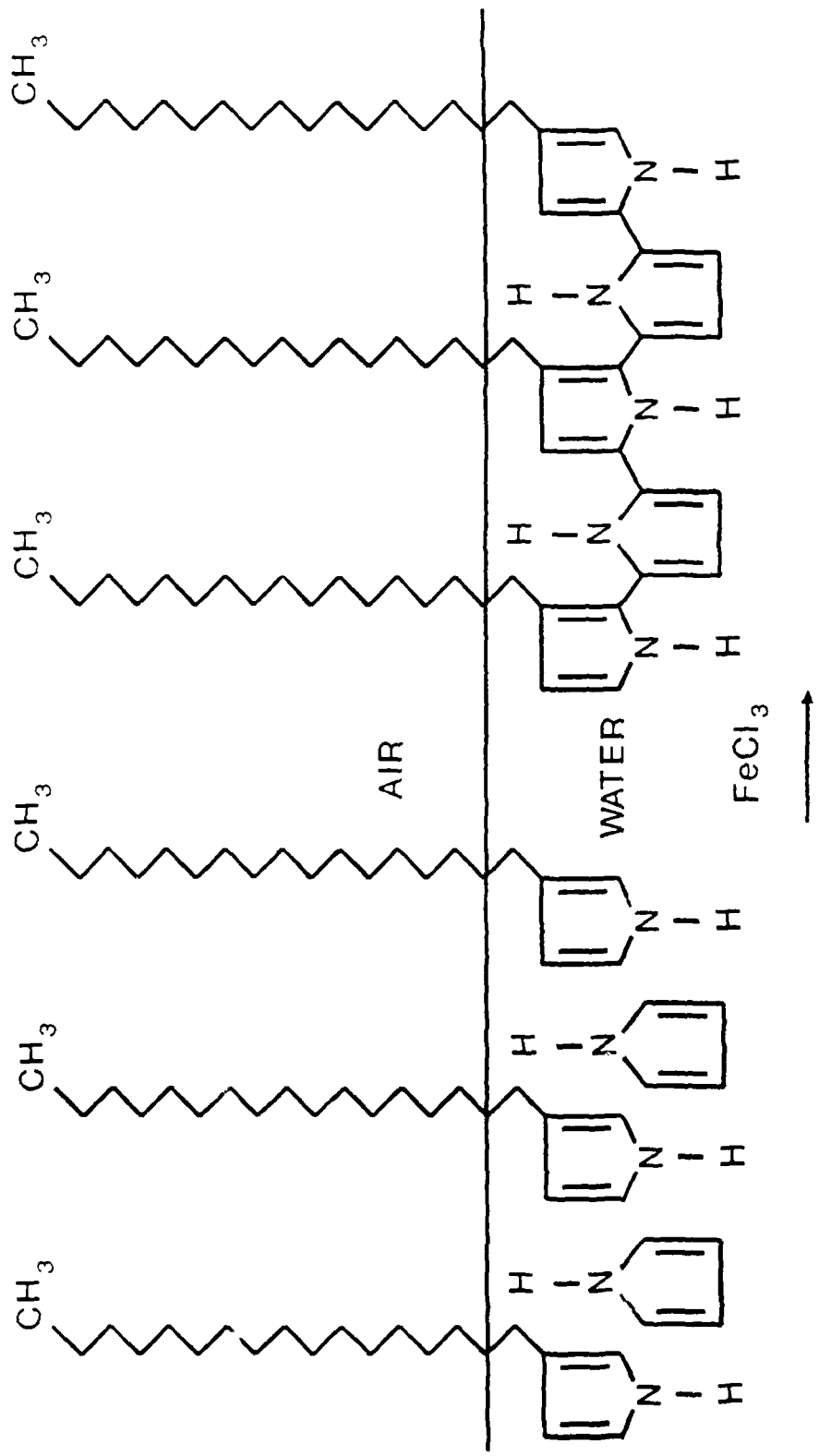
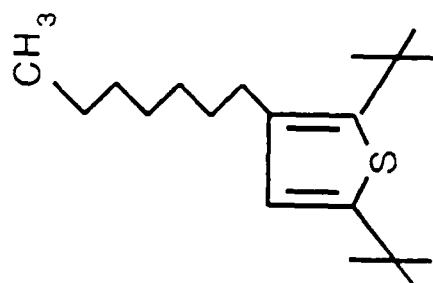


Figure 1
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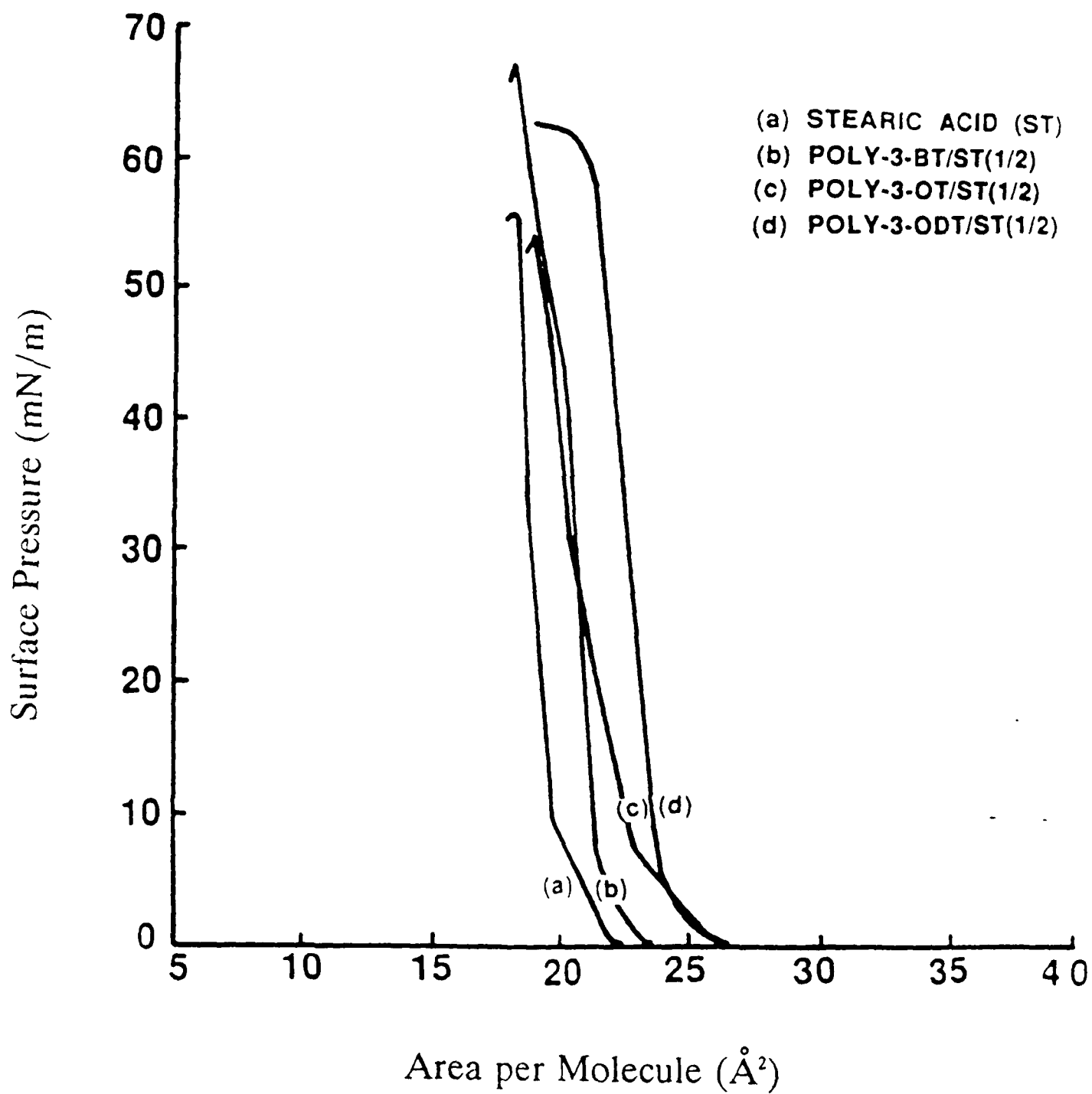


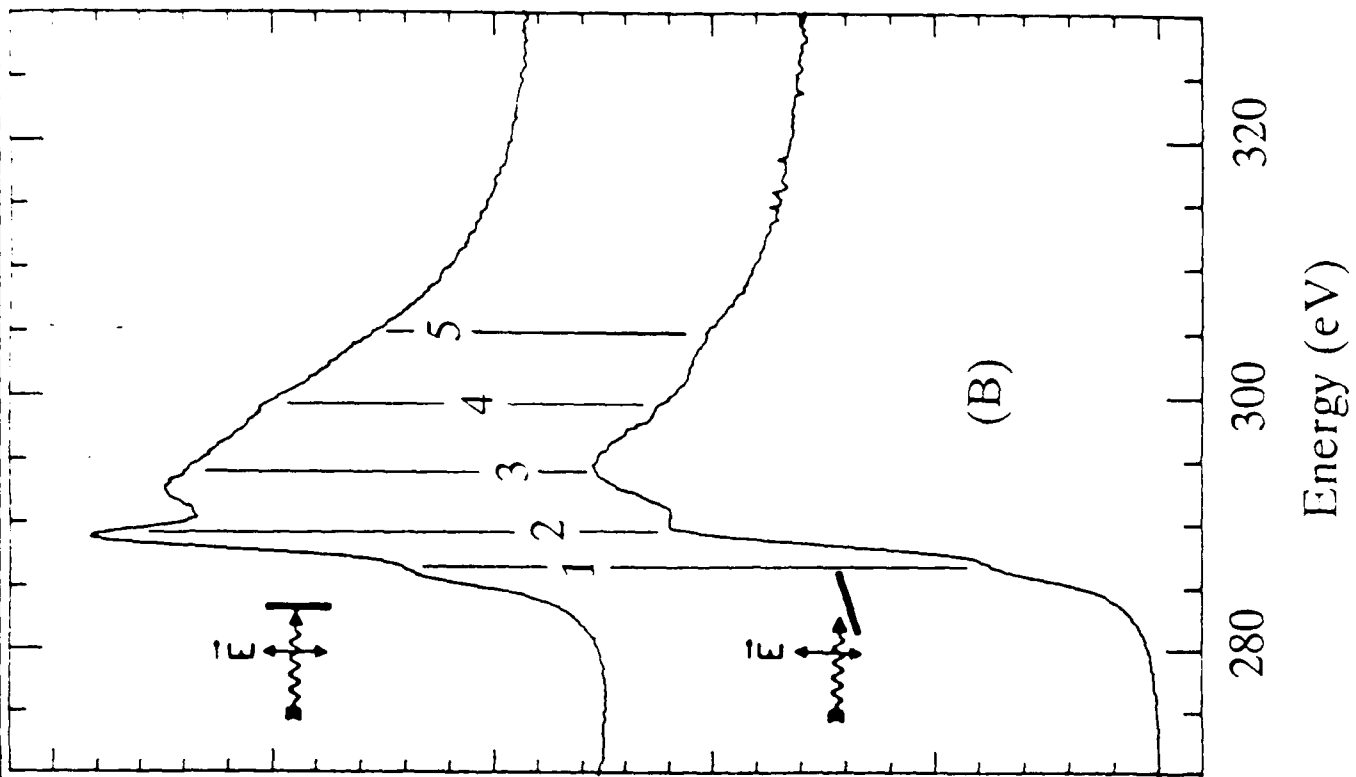
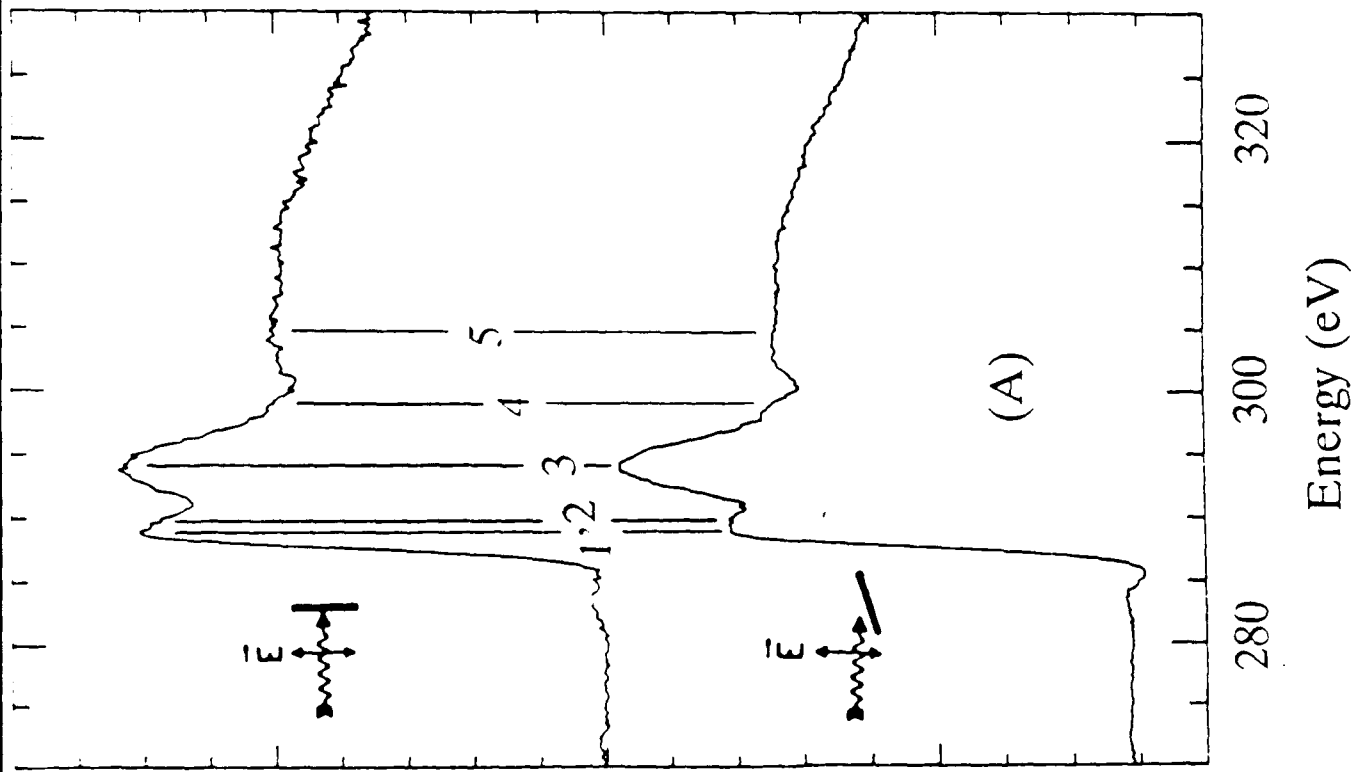


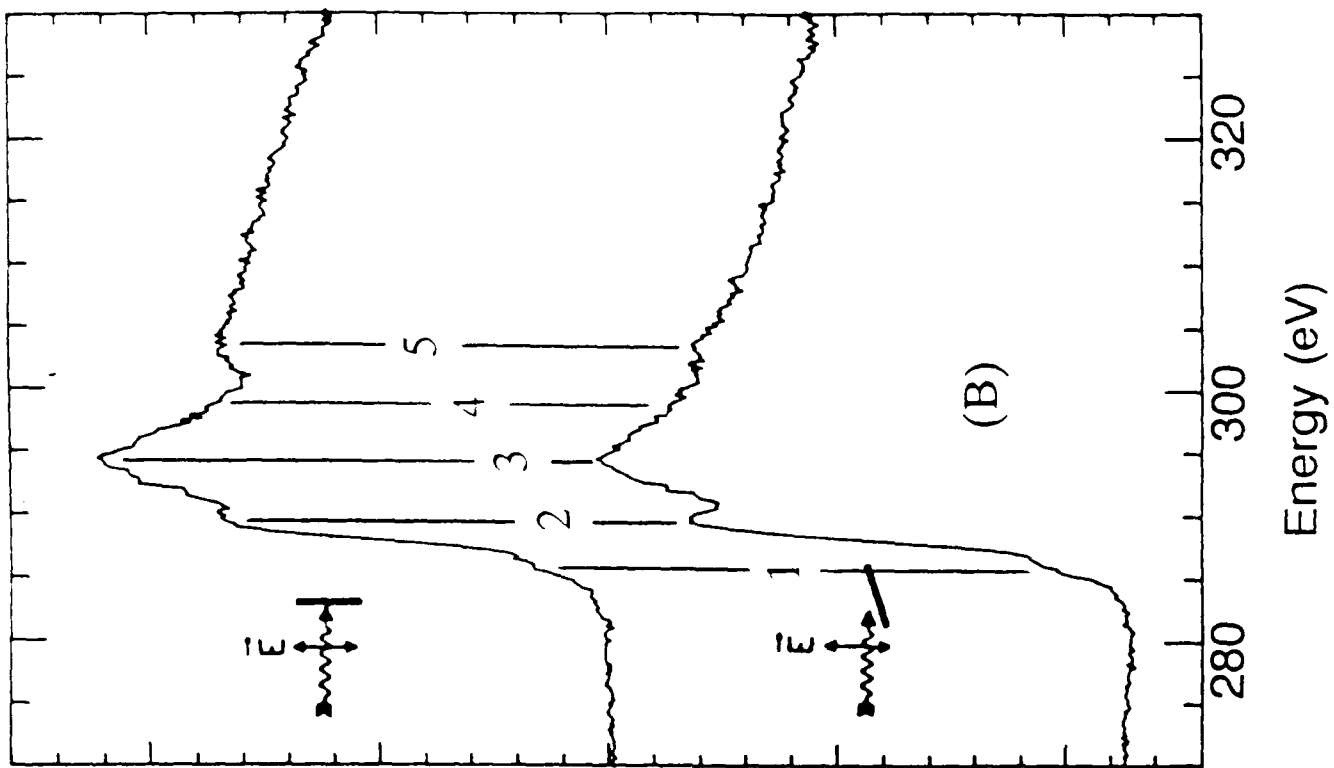
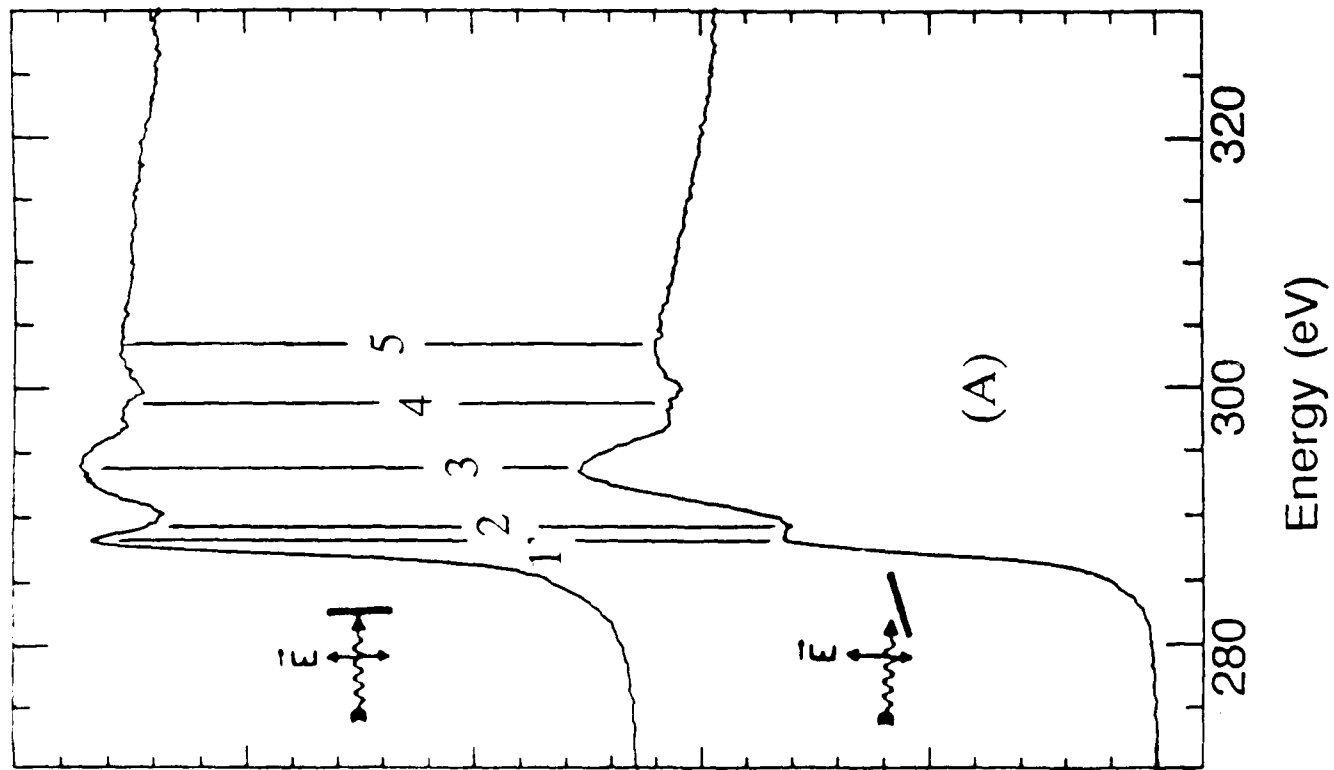
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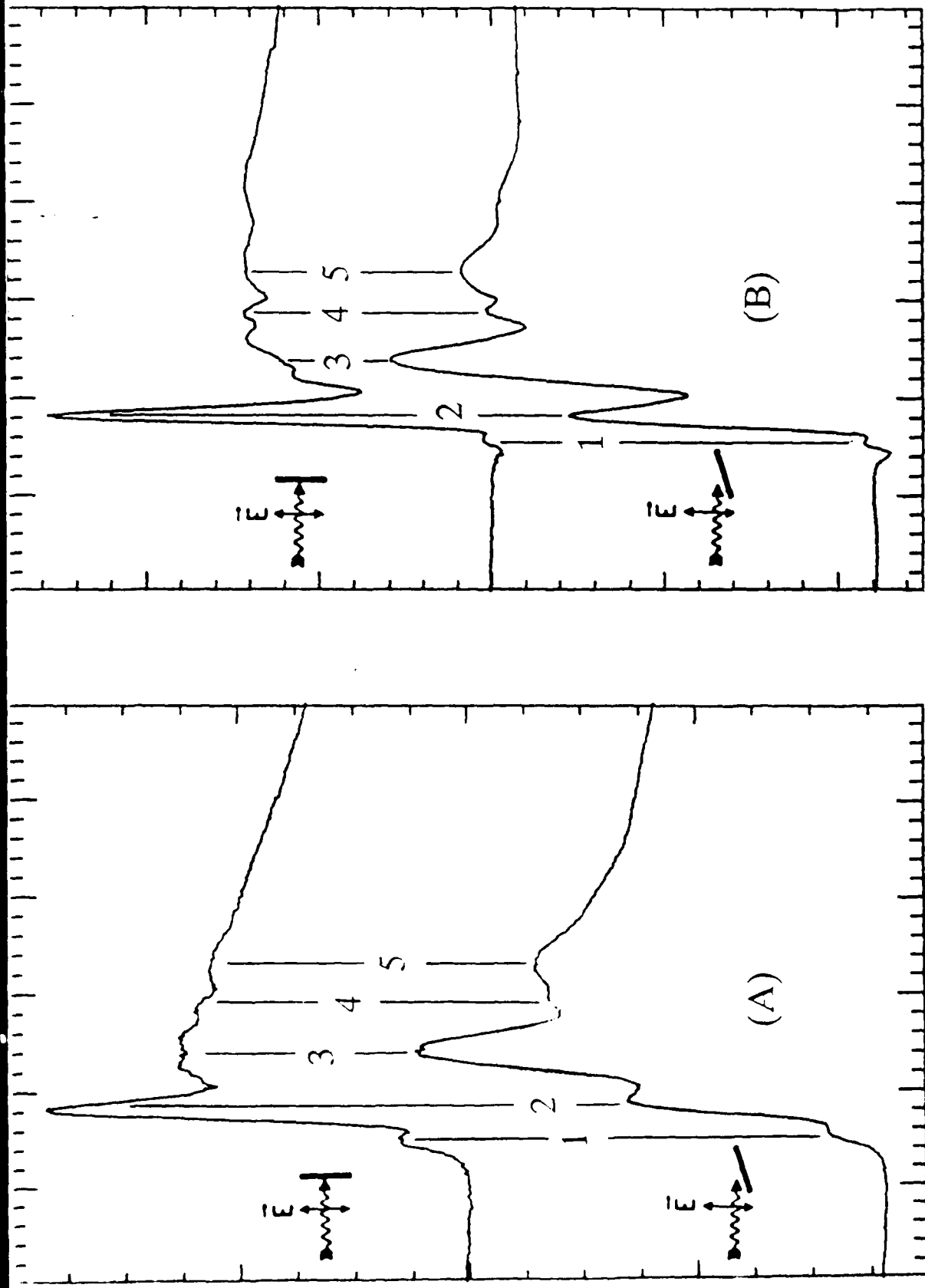


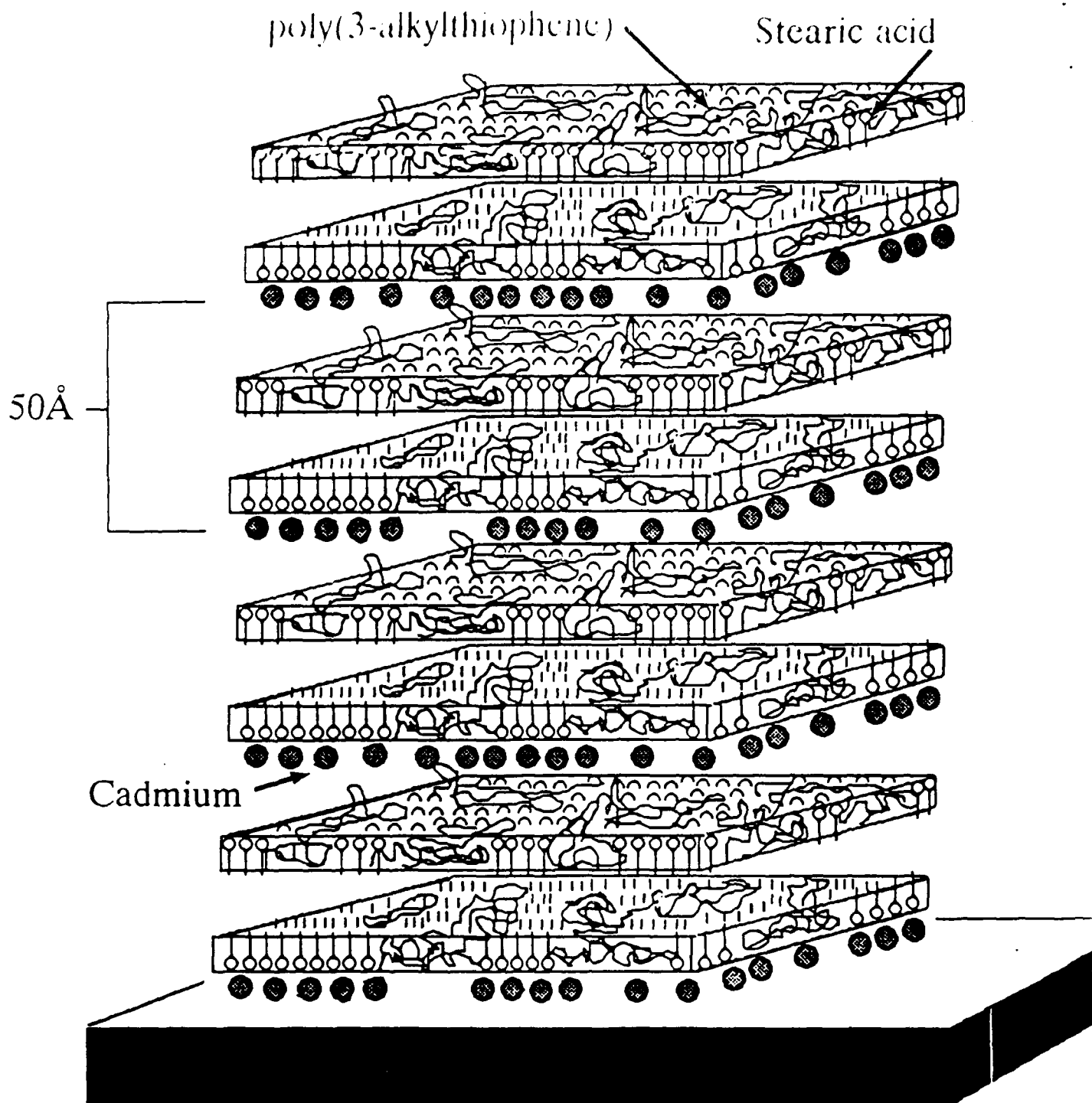
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**Structure of mixed stearic acid/poly(3-alkylthiophene)
LB Film**

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